Heliyon

Received:
16 September 2016
Revised:
12 December 2016
Accepted:
5 January 2017

Heliyon 3 (2017) e00232

Ambient aging of rhenium filaments used in thermal ionization mass spectrometry: Growth of oxo-rhenium crystallites and anti-aging strategies

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Abstract

Degassing is a common preparation technique for rhenium filaments used for thermal ionization mass spectrometric analysis of actinides, including plutonium. Although optimization studies regarding degassing conditions have been reported, little work has been done to characterize filament aging after degassing. In this study, the effects of filament aging after degassing were explored to determine a "shelf-life" for degassed rhenium filaments, and methods to limit filament aging were investigated. Zone-refined rhenium filaments were degassed by resistance heating under high vacuum before exposure to ambient atmosphere for up to 2 months. After degassing the nucleation and preferential growth of oxo-rhenium crystallites on the surface of polycrystalline rhenium filaments was observed by

http://dx.doi.org/10.1016/j.heliyon.2017.e00232

atomic force microscopy and scanning electron microscopy (SEM). Compositional analysis of the crystallites was conducted using SEM-Raman spectroscopy and SEM energy dispersive X-ray spectroscopy, and grain orientation at the metal surface was investigated by electron back-scatter diffraction mapping. Spectra collected by SEM-Raman suggest crystallites are composed primarily of perrhenic acid. The relative extent of growth and crystallite morphology were found to be grain dependent and affected by the dissolution of carbon into filaments during annealing (often referred to as carbonization or carburization). Crystallites were observed to nucleate in region specific modes and grow over time through transfer of material from the surface. Factors most likely to affect the rates of crystallite growth include rhenium substrate properties such as grain size, orientation, levels of dissolved carbon, and relative abundance of defect sites; as well as environmental factors such as length of exposure to oxygen and relative humidity. Thin (~180 nm) hydrophobic films of poly(vinylbenzyl chloride) were found to slow the growth of oxo-rhenium crystallites on the filament surfaces and may serve as an alternative carbon source for filament carburization.

Keywords: Materials Science

1. Introduction

Rhenium has been used widely as an ionization surface in thermal ionization mass spectrometry (TIMS) for isotopic analysis of plutonium [1, 2]. Rhenium is the preferred material in these analyses for its high work function and melting point that is well above ionization temperatures for plutonium [3]. Rhenium also has been employed as an ionization surface for a variety of other analytes [4, 5, 6, 7, 8]. The use of rhenium in other high-temperature applications has been limited by its oxidation characteristics [9]. It readily oxidizes above 600 °C when exposed to atmospheric oxygen and water vapor [10, 11]. High vacuum, thus low oxygen partial pressure, environments produced in TIMS systems are what enable the successful use of rhenium as a thermal ionization filament. Despite its susceptibility to oxidation and terrestrial scarcity, rhenium has remained an important material in the production of turbine blades [12], catalysts [13], and heating elements [14]; consequently, rhenium has been the subject of scientific investigations for many decades [15, 16, 17, 18, 19, 20, 21, 22, 23]. Despite these efforts, little is known about the chemical identities of species involved in catalytic [24] and surface ionization mechanisms [25, 26] due to the challenges associated with *in-situ* analysis.

Over decades of use in TIMS systems, various pretreatment methods for rhenium filaments have been developed to improve ionization efficiency [7, 27, 28, 29]. The most common of these pretreatment methods is known as “degassing” or “outgassing” of filaments prior to sample loading and analysis. Degassing involves

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